Design of a Tandem Conjugated Polymer Bulk Heterostructure Solar Cell

J. Valenzuela, S. Mil'shtein
Advanced Electronic Technology Center
ECE Dept, UMass, Lowell, 01854, USA. Sam_Milshtein@uml.edu

ABSTRACT

The design of a conjugated polymer-based multilayered solar cell is presented. The device, comprised of layers of bulk heterojunctions, takes advantage of the diverse absorption characteristics of the materials involved to improve efficiency. 100nm layers of poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1-4-phenylene vinylene]: phenyl C61-butyric acid methylester MDMO-PPV:PCBM (1:4), (poly-3-hexylthiophene):phenyl C61-butyric acid methylester P3HT:PCBM (1:1) and poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopen[2,1-*b*;3,4-*b*′]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] PCPDTBT:PCBM (1:3), are designed to be connected using transparent cathodes of lithium fluoride/aluminum/gold LiF/Al/Au, which are compatible with PCBM LUMO. Studies on the effects of insertion of identical sub-cells, thermal, electrical and solvent annealing is also considered.

***Keywords*:** solar, heterojunction, conjugated, polymer, tandem

1 INTRODUCTION

The use of conjugated polymers in solar cell applications has drawn a lot of attention as a way of bringing the high cost of electricity produced by inorganic solar cells to competitive levels. Different research groups have fabricated conjugated polymer solar cells which demonstrated efficiencies about 5%, mainly due to the limited characteristics of the materials, namely mobility and absorption coefficient [1]. Limited exciton, and free carriers, diffusion lengths on these materials have been the main reason for low efficiency. It has been established that excitons in conjugated polymers have a diffusion length of approximately 10nm. The nature of excitons requires that energy levels present at an interface be bigger than the binding energy of the exciton. In this regard, the use of heterostructure p-n junction carries significant improvement due to secure charge dissociation and transfer. To the lesser extent this advantage exists in a Donor-Acceptor (D/A) bulk polymer heterojunctions. Free carrier diffusion lengths keep the available thickness of the active layers limited to a 100-200nm range. However in such a thin layer the amount of light that can be absorbed by their polymer mixtures only amounts to 50% [2]. That reduces the device's ultimate efficiency.

2 TANDEM CONFIGURATION

The search for low bandgap conjugated polymers has been a focus of intense research in the last couple of years. Processing limitations along with poor electrical characteristics left these materials with low efficiency for all solar cell applications. Unlike inorganic materials, conjugated polymers have a pronounced frequency dependant absorption characteristic. This makes a multilayer approach more suitable for design of cells with big absorption and at the same time generation of large amounts of charge.

Selection of the right materials targets a coherent distribution of energy and absorption levels in the device. In tandem configuration, the generated current of the whole device is limited by the presence of its less productive layer [3]. It is the low mobility of that layer is of major concern.

Several of the studies conducted with different donors in active layers have shown that lower bandgaps translate into higher photocurrents [4, 5]. Therefore, in a tandem configuration, the

Clean Technology 2008, www.ct-si.org, ISBN 978-1-4200-8502-0

limiting current will most likely come from the biggest bandgap material.

3 MATERIALS

From the commercially available conjugated polymers, MDMO-PPV, P3HT and PCPDTBT with electrical bandgaps of 2.2, 1.9 and 1.46 electron volts respectively have been extensively used in single layer bulk heterojunction solar cells. In the case of (1:4) mixture MDMO-PPV:PCBM bulk heterojunctions have shown a short circuit current of about 8mA/cm^2 [6], which is comparable to the 10mA/cm^2 obtained, under similar circumstances (100mW/cm^2), for (1:1) P3HT:PCBM heterojunctions devices. The current of 16mA/cm^2 has been obtained in devices using (1:3) PCPDTBT:PCBM mixtures [7]. Therefore, any tandem configuration considering these 3 layers, will have the current generated in the PCPDTBT:PCBM layer limited to a percentage of its potential value, reducing the expectations of efficiency values as reported for a single layer devices of that mixture.

To ensure a proper utilization of the available light, in tandem configurations, efficient transparent cathodes are needed. Shrotriya [8] demonstrated that LiF/Al/Au transparent cathodes can be used for tandem configurations allowing a high percentage of light, at most of the sun's spectra frequencies, to be transmitted to subsequent layers. These cathodes provide energy levels compatible with PCBM, the most used acceptor in bulk heterojunctions. Employing semitransparent cathodes, allows to build individual cells with diverse active layers. From the standpoint of processing methods the best suggestion is to bring the layers together after each of them had polymerized.

As far as doping is concerned, the principal acceptor used in conjugated polymer solar cells is the fullerene PCBM. Its low electron acceptance time, LUMO-HOMO levels and its positive effect on the donor's hole mobility [9], makes PCBM a perfect candidate for charge dissociation and collection. Within the PCBM family, [60] PCBM is selected, due to the superior qualities shown when in D/A mixtures [10].

4 DESIGN

After intense analysis of the literature we came to the conclusion that the solar cell with higher efficiency should carry 3 layers which were carefully selected by our group. We also took into account the complexity of the synthesis of these materials in attempt to optimize the cost of the final product.

Due to the current limitation presented by PCBM:MDMO-PPV layers, the goal of this design is to obtain at least 9mA/cm^2 of short circuit current density on all our layers. For this, the concentration of PCBM and thickness of the active layer need to be chosen accordingly.

Dennler [11] showed that increasing the PCBM concentration in the mixture of PCBM:MDMO-PPV increases dramatically the mobility of free carriers. However, when PCBM concentrations go over 90%, morphology problems arise, limiting not only mobility [12] but absorption properties as well [13]. Also, as Hoppe demonstrated [2], MDMO-PPV:PCBM active layers yield to better internal quantum efficiency when limited to a 100nm thickness. In an analogous way, P3HT:PCBM mixtures showed a better quantum efficiency when in (1:1) ratio [14] with optimal thickness, for a 10mA/cm^2 density current, between 76 and 84nm [15]. Similarly, PCPDTBT:PCBM layers have shown current densities of 9.2mA/cm^2, with a required thickness of less than 130nm [16]

Therefore, the active layer portion of the design has been chosen as follow:

- Front Cell: MDMO-PPV:PCBM (1:4) 100nm
- Middle Cell: P3HT:PCBM (1:1) 100nm
- Bottom Cell: PCPDTBT:PCBM (1:3) 100nm

When it comes to electrodes, it has been shown that, for anodes, the thickness of a PEDOT:PSS layer on an ITO/ PEDOT:PSS arrangement, has no real impact on the overall efficiency [17]. For cathodes, the need to transmit light through the electrode to the subsequent layers, requires

transparent materials. LiF(1nm)/Al(2.5nm)/Au (12.5nm) cathodes have been used successfully, showing higher levels of transparency when compared to regular semitransparent electrodes [7].

- Anodes: ITO/PEDOT:PSS
- Middle Cathodes: LiF(1nm)/Al(2.5nm) /Au(12.5nm)
- Bottom Cathode LiF/Al

Figure 1, shows the physical structure of the solar cell and the arrangement of layers from the top to the bottom.

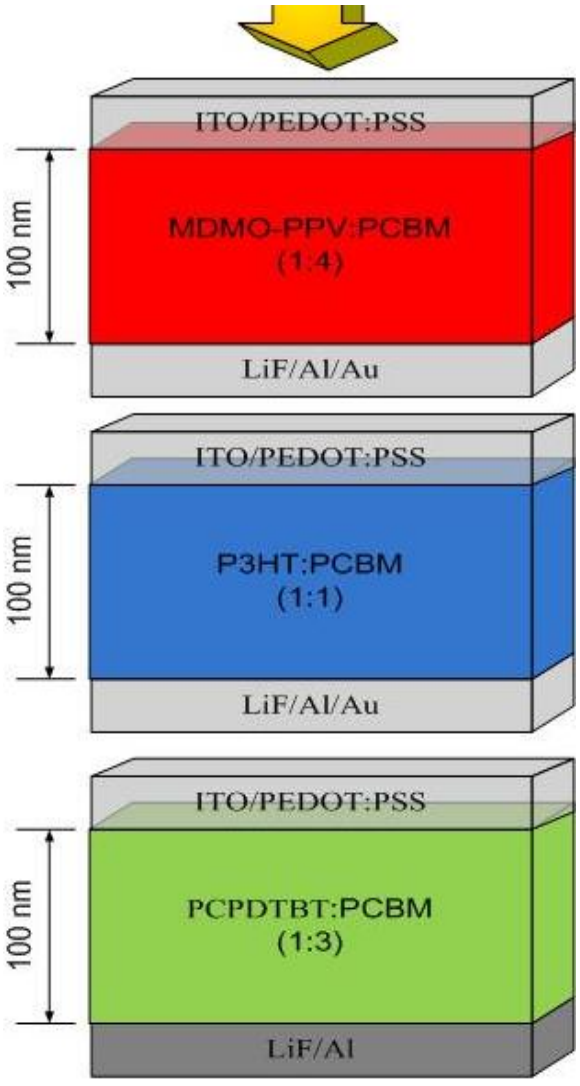

Figure 1: Schematic diagram of the proposed design.

5 FABRICATION

The use of transparent cathodes allows a simpler fabrication process. Under these conditions, each layer can be processed separately, avoiding the potential damage to other layers by the solvents used. This not only allows a better post-treatment, as thermal and electrical annealing, but also allows the use of solvent annealing. The annealing of solvent is expected to improve the design structure of the materials after polymerization [18]. The use of chlorobenzene as a solvent for the PCBM:MDMO-PPV and P3HT:PCBM layers processing, has shown better short circuit current densities, maintaining the open circuit voltage, leading to better efficiencies [19-20]. The addition of 2.5 % of alkanedithiols (octanedithiol) to chlorobenzene has shown improvement on the fill factor for PCPDTBT:PCBM layers, providing a shift of absorption of the mixture to the NIR part of the spectra. Analysis of the effect of these additives will be conducted on the PCBM:MDMO-PPV and P3HT:PCBM layers to evaluate its effect on the overall efficiency.

6 CONCLUSION

The design of a novel tandem solar cell has been presented. The frequency dependant absorption characteristics of all three layers in our design are complimentary each to the other. In addition, these materials are commercially available. The use of transparent cathodes with transparency levels of 70% on most of the frequency spectra, allowed the design with multiple layers. Based on the reported performance [8] of the individual layers and the cathodes transparency characteristics, we predict that our design should have at least 6-7% efficiency. Electrical, thermal and solvent annealing will be also conducted. In our future work we plan to redesign the existing cell. For each of the three layers we would add a second layer of the same material properties back to back but separated by transparent contacts. This structure will allow to increase absorption of light of every given part of the light spectrum. So

Clean Technology 2008, www.ct-si.org, ISBN 978-1-4200-8502-0

at the end, the thickness of each layer would be doubled and the total sandwich will comprise of six polymer layers. The implementation and production of the novel design will be our next step as well.

7 REFERENCES

[1] Hoppe, H., Sariciftci, N., S., "Polymer Solar Cells", Advances in Polymer Science, October, 2007, ed. by S. Marder and K.-S. Lee, Springer (Berlin, Heidelberg), on-line available

[2] H. Hoppe et Al, "Modeling of optical absorption in conjugated polymer/fullerene bulk-heterojunction plastic solar cells", Solar Energy Materials & Solar Cells Vol. 80, 105-113, (2003)

[3] A. Hadipour et Al, "Solution-Processed Organic Tandem Solar Cells", Advanced Functional Materials, Vol. 16, No. 14, pp. 1897-1903, 2006

[4] Mihailetchi, V. D. et Al, "Charge Transport and Photocurrent Generation in Poly(3-hexylthiophene): Methanofullerene Bulk-Heterojunction Solar Cells", Advanced Functional Materials, Vol. 16, No. 5, pp. 699-708, 2006

[5] Soci, C., "Photoconductivity of a Low-Bandgap Conjugated Polymer, Advanced Functional Materials", Vol. 17, No. 4, pp. 632-636, 2007

[6] Hoppe H., Sariciftci, N. S., "Morphology of polymer/fullerene bulk heterojunction solar cells", J. Mater. Chem., 2006, 16, 45 - 61

[7] Peet, J. et Al, "Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols", Nature Materials 6, 497 - 500 (2007)

[8] Shrotriya, V., et Al, "Transition metal oxides as the buffer layer for polymer photovoltaic cells", Appl. Phys. Lett. 88, 073508 (2006) (SCI)

[9] Melzer, C., et Al, "Hole Transport in Poly(phenylene vinylene)/Methanofullerene Bulk-Heterojunction Solar Cells", Advanced Functional Materials, Vol 14, No. 9, pp. 865-870, 2004

[10] Kooistra, F. B., "Fullerenes for Organic Electronics", PhD. Thesis, Zernike institute of Advanced Materials, University of Groningen, Nov. 2007

[11] Dennler, G., et Al, "Charge carrier mobility and lifetime versus composition of conjugated polymer/fullerene bulk-heterojunction solar cells, Organic Electronics", Vol. 7, Issue 4, pp. 229-234, 2006

[12] Pacios, R. et Al, "Efficient Polyfluorene Based Solar Cells", Synthetic Metals, Volume 137, Issues 1-3, 4 April 2003, Pages 1469-1470

[13] Goris, L. et Al, "Absorption phenomena in organic thin films for solar cell applications investigated byphotothermal deflection spectroscopy", Journal Of Materials Science, Vol. 40, pp. 1413–1418, 2005

[14] Hayashi, Y., et Al, "Investigation of PCBM concentration on photovoltaic characteristics of polymer solar cells with blends of p3ht and PCBM", Photovoltaic Energy Conversion, Conference Record of the 2006 IEEE 4th World Conference on, Vol. 1, pp. 271-274, 2006

[15] Sylvester-Hvid, K. O. et Al, "Analyzing poly (3-hexyl-thiophene):1-(3-methoxy-carbonyl) propyl-1-phenyl-(6, 6) C [sub 61] bulk-heterojunction solar cells by UV-visible spectroscopy and optical simulations", J. Appl. Phys. 102, 054502 (2007), DOI:10.1063/1.2775219

[16] Kim, J. Y., et Al, **"**Efficient Tandem Polymer Solar Cells Fabricated by All-Solution Processing", Science, Vol. 317. no. 5835, pp. 222 – 225, 2007

[17] Zhou, Y., et Al, "Mild oxygen plasma treated PEDOT:PSS as anode buffer layer for vacuum deposited organic light-emitting diodes", Chemical Physics Letters, 427 (2006)

[18] Li, G. et Al, ""Solvent Annealing" Effect in Polymer Solar Cells Based on Poly(3-hexylthiophene) and Methanofullerenes", Advanced Functional Materials, Volume 17, Issue 10 , pp. 1636 - 1644

[19] Al-Ibrahim, M., et Al, "Effects of solvent and annealing on the improved performance of solar cells based on poly (3-hexylthiophene):Fullerene", Appl. Phys. Lett. 86, 201120, 2005

[20] Rispens, M. T. et Al, "Influence of the solvent on the crystal structure of PCBM and the efficiency of MDMO-PPV:PCBM 'plastic' solar cells", Chem. Commun., pp. 2116 – 2118, 2003